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Candidate session number

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Examination session (May or November)

May

Year

2015

Diploma Programme subject in which this extended essay is registered:

Chemistry

(For an extended essay in the area of languages, state the language and whether it is group 1 or group 2.)

Title of the extended essay: Comparison Between the Effects of the Addition of Various Cations via Salt Solution on the Aggregation of Silver Nanoparticles Synthesized via the Reduction Method

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The extended essay I am submitting is my own work (apart from guidance allowed by the International Baccalaureate).

I have acknowledged each use of the words, graphics or ideas of another person, whether written, oral or visual.

I am aware that the word limit for all extended essays is 4000 words and that examiners are not required to read beyond this limit.

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Date: Feb 4th 2015

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_____ had previously taken a summer course in material science, and had clear idea that he would like to work on a "modern" material in this Extended Essay in Chemistry. He investigated a wide range of substances (e.g., quantum dots, hydrogels), both through review of the primary literature (e.g., *J. Chem. Ed.*, *Science*, and other periodicals we have a subscription to) and hands-on trial in the laboratory. _____ initiated correspondence with _____ of R _____ University, the professor in the previous short course, during the initial phase, who suggested the possibility of modelling the nanoparticle sizes mathematically; _____ would proceed to research the method himself.

_____ was organized, competent, and detail-oriented in the lab. The silver nanoparticles he looked at were fidgety to get right at the beginning, and _____ did a good job in working out the technical difficulties. There were *many* samples generated, which he kept in meticulous order. _____ discovered the limitations of our visible light spectrometer (and software) only half-way through, but managed to overcome both by intelligent workarounds. He supplemented this with mathematical fitting / modelling of the particles, and the result is a dense, complete treatment of his research topic.

It had been a pleasure supervising _____. He is enthusiastic about this work, and clearly engaged. He attended all the meetings with full readiness, and completed drafts at agreed upon deadlines. This final draft is in line with previous drafts I have seen and authentically his own work.

I have read the final version of the extended essay that will be submitted to the examiner.

To the best of my knowledge, the extended essay is the authentic work of the candidate.

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I spent 5 hours with the candidate discussing the progress of the extended essay.

Supervisor's signature: _____

Date: 28 FEB 2015

Assessment form (for examiner use only)

Candidate session number

Achievement level

Criteria	Examiner 1	maximum	Examiner 2	maximum	Examiner 3
A research question	2	2		2	
B introduction	1	2		2	
C investigation	4	4		4	
D knowledge and understanding	4	4		4	
E reasoned argument	4	4		4	
F analysis and evaluation	3	4		4	
G use of subject language	4	4		4	
H conclusion	2	2		2	
I formal presentation	4	4		4	
J abstract	2	2		2	
K holistic judgment	4	4		4	
Total out of 36	34				

Name of examiner 1: _____ Examiner number: _____
(CAPITAL letters)

Name of examiner 2: _____ Examiner number: _____
(CAPITAL letters)


Name of examiner 3: _____ Examiner number: _____
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Extended Essay

Comparison Between the Effects of the Addition of Various Cations via Salt Solution on the Aggregation of Silver Nanoparticles Synthesized via the Reduction Method



Subject: Chemistry

Word Count: 3981

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Abstract:

which ones

This experiment investigated the following research question: "How does the addition of different cations via salt solution affect the rate and overall degree of aggregation of silver nanoparticle solution synthesized via the reduction method?" *mg*

Silver nanoparticles are formed when a solution of silver precursor, such as AgNO_3 , is mixed with a strong reducing agent, such as NaBH_4 . The agent reduces silver ions into neutral atoms, which then clump together in a process called aggregation. Excess BH_4^- anions then form an electrostatic repulsive barrier around the newly created silver nanoparticles, preventing further aggregation. The presence of hydrated cations in the addition of salt solution inhibits these charges and allows aggregation to continue. While it is well documented in literature that adding salt solution would cause aggregation, comparisons between different types of salt solutions are not.¹ The lack of literature in this area as well as the growing interest in nanoparticles and nanotechnology within the scientific community has led me to investigate this research question. *m*

In this experiment, 0.2 mL 0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M of LiCl , KCl , NH_4Cl and NaCl salt solutions were added to 3mL samples of silver nanoparticle solutions. The resulting size of the aggregated nanoparticles was calculated through the analysis of an absorbance spectrum measured by a spectrometer, recorded a minute after addition of salt solution. Rate of aggregation is also compared by contrasting relative absorbance at wavelength $\lambda = 407.0 \text{ nm}$. It is found that an increase in ionic strength leads to an increase in both rates of aggregation as well as overall degrees of aggregation. KCl is noted to cause the greatest degree of aggregation and highest rate of aggregation, followed by NH_4Cl , NaCl and finally LiCl . Ionic strength is found not to be the defining factor in determining aggregation. *c*

Word Count: 298

¹ (Alzoubi, F. Y.)

Research Question

How does the addition of different cations via salt solution affect the rate and overall degree of aggregation of silver nanoparticle solution synthesized via the reduction method?

Introduction

Nanoparticles are defined to be particles in which one or more dimensions are between 1-100 nm in size. Their unique size effectively makes them a bridge between molecular structures and bulk materials, sharing certain properties of both. For example, unlike bulk materials, certain properties, such as their optical properties, exhibited by nanoparticles are often dependent on size and shape. Gold nanoparticles, for instance, dispersed within a solution exhibit variations in colour depending on their diameter, starting from a bright red colour and turning into dark purple as the particle size increases, despite the fact that in bulk gold is golden in colour, illustrated in figure 1.

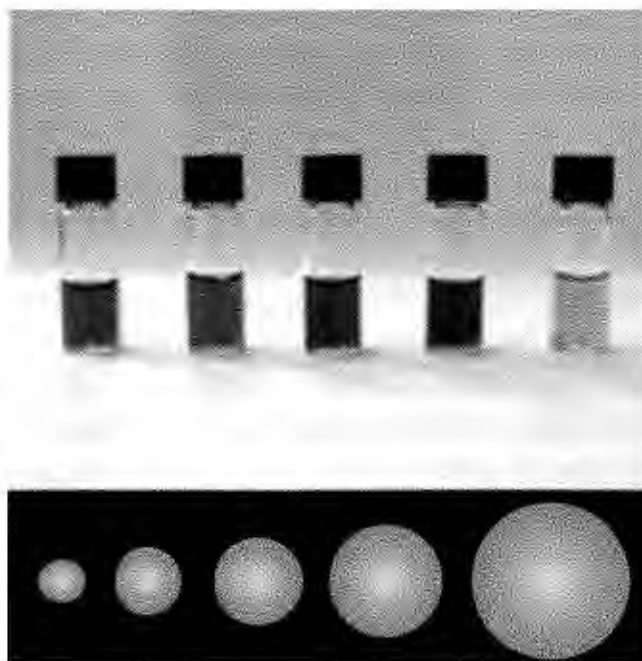


Figure 1. Picture showing colour change shifts from red to purple as gold nanoparticle diameter increases (smallest ~5 nm to largest ~100 nm).

Nanoparticles are currently the subject of immense scientific interest due to their industrial uses in a wide variety of fields. Silver nanoparticles have been noted to exhibit anti-bacterial effects, and is effectively utilized in medical treatment.² Titanium oxide nanoparticles have been used as potent UV-scatters

² "Silver Nanoparticle Properties."

in sunscreen.³ Nanoparticles have even been used in clinical trials in cancer-therapy by colour-marking cancer cells.⁴

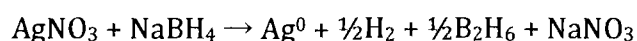
It is clear that many of properties that make nanoparticles so useful are due to its size. From this, I have decided to focus my extended essay on aggregation, because while it is known that the addition of salt solution would cause aggregation, little is known about the effects on aggregation varying the salt solution would have. This experiment could bring about greater understanding regarding the processes of aggregation.

Background Information

The Reduction Method

The reduction method is a bottom-up approach to synthesizing nanoparticles, in which nanoparticles are 'grown' from their smaller individual atoms. This method is especially useful in the synthesis of metallic nanoparticles due to its ease, low cost, controllability, and simple indication on whether synthesis is successful.⁵

Synthesis of silver nanoparticles by the reduction method begins with a solution of silver nitrate (AgNO_3), to which a solution of *excess* sodium borohydride (NaBH_4) is mixed. The solutions undergo the following redox reaction:



In which the Ag^+ ions in AgNO_3 are reduced into neutral Ag^0 atoms.

The reaction leads to an accumulation of Ag^0 atoms within the solution, eventually reaching the saturation limit. To prevent super-saturation, the Ag^0 atoms then undergo nucleation to create clusters, in which up to twelve atoms are forced to stick together through Van Dal Waal's forces. From there, these clusters stick with other clusters and grows in size, a process we call aggregation.

In this particular case, sodium borohydride also acts as a surfactant. Once the silver nanoparticles has aggregated to a certain size, excess NaBH_4 will act as a surfactant, adsorbing to each nanoparticle with a number of BH_4^- anions, preventing further aggregation as the BH_4^- anions would repel each other by repulsive electrostatic forces.

³ (Todorov, G.)

⁴ (Setua, Sonali)

⁵ (Lamer, Victor K.)

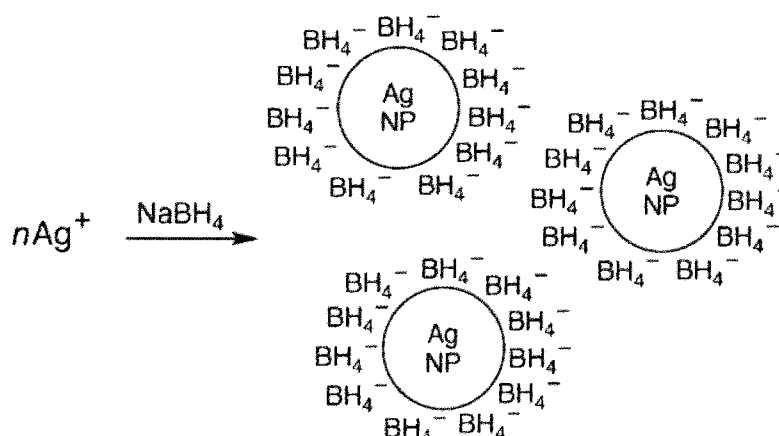


Figure 2. Diagram showing adsorbed borohydride separating silver nanoparticles by repulsive forces⁶

Localized Surface Plasmon Resonance (LSPR)

Monodispersed silver nanoparticles have the unique optical property in that as the nanoparticles aggregate, the colour of the solution darkens from a bright yellow into dark grey. This optical property is due to localized surface plasmon resonance.

Localized surface plasmon resonance is the collective oscillation of electrons on a metallic nanoparticle due to light. When light hits a metallic nanoparticle, the electrons on the nanoparticle delocalize and oscillate at a certain frequency, forming an electric field opposite to that of the light wave, thereby absorbing electromagnetic waves with equal frequency. These oscillations are sensitive to its environment, such as the medium in which the nanoparticles are dispersed and, most importantly, the size of the particle. For nanoparticles, the size is often just right that the localized surface plasmon resonance happens to oscillate in the wavelength of visible light, and thus absorbing that wavelength of light. This causes a colour change in the solutions of dispersed nanoparticles.

⁶ (Solomon, Sally D.)

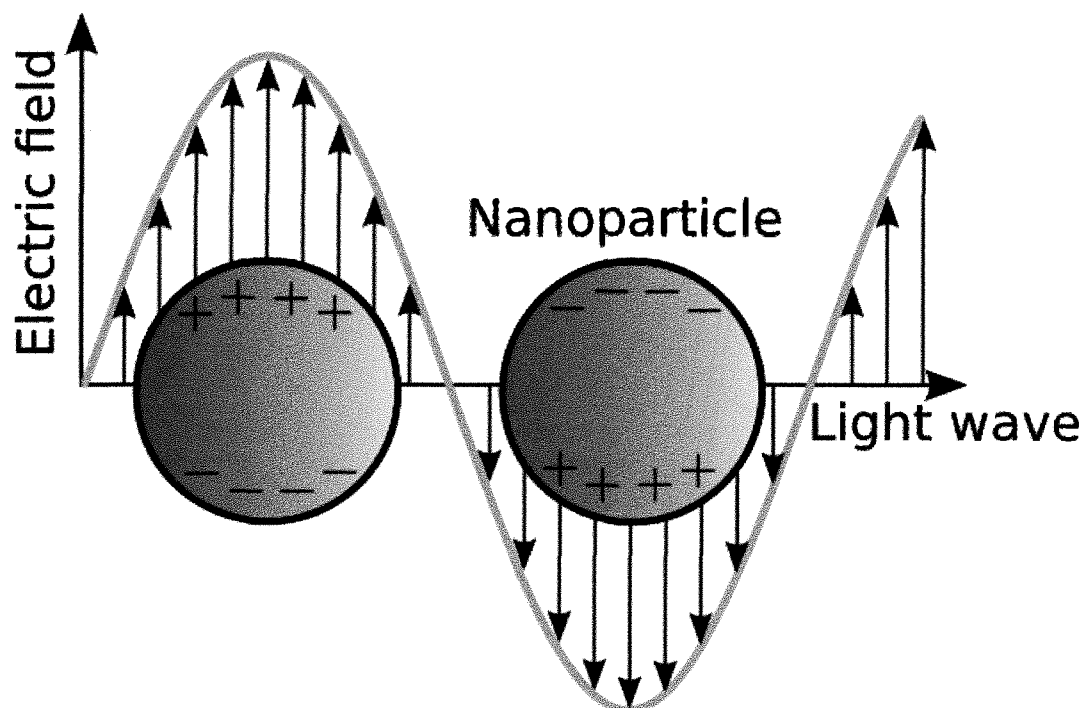


Figure 3. Demonstration of oscillating charges on the nanoparticle resulting in electric fields due to energy from light waves?

Because size is the main factor in determining the wavelength caused by LSPR, it becomes clear that by studying the absorption spectra of a solution, the size of the nanoparticle can be derived. This is especially important as this allows a method to determine the size of my synthesized nanoparticles with a visible-light spectrometer, which is commonly available to high school laboratories.

Determining Aggregation

Due to the localized surface plasmon resonance of silver nanoparticles, as aggregation occurs due to the addition of salt solution, the colour of the nanoparticles change from light yellow to dark yellow to light grey.

An UV-spectrometer can be used to find the absorption spectrum of the nanoparticle solution, which can then be used to deduce the size of the nanoparticles. As aggregation and thus particle size increases, the absorbance peak redshifts to higher wavelengths as well as lowers in its peak, as seen in Figure 4.

⁷ "Nanoparticle Plasmonics."

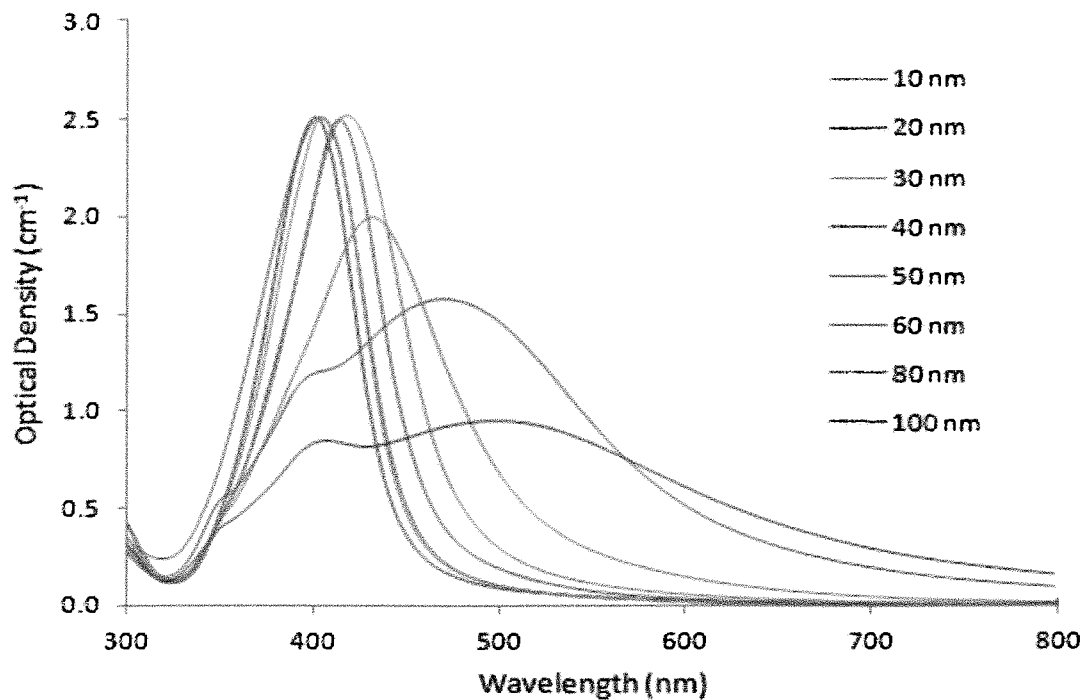


Figure 4. UV-Spectra of silver nanoparticles at different sizes⁸

Literature suggests that, given the absorption spectrum, one can quantitatively deduce the nanoparticle size using a special subset of Mie's Scattering Theory:

$$w = \frac{(\epsilon_0 + 2n^2)cmu_F}{2N_c e^2 D}$$

Where w is the full width at half maxima peak of the spectrum, D is the diameter of the nanoparticle, and ϵ_0 , n , c , m , u_F , N_c , and e represent the frequency independent part of complex form of dielectric constant, refractive index of water, velocity of light mass of electron, electron velocity at the Fermi energy number of electrons per unit volume, and the electron charge, respectively.⁹

However, there are technical limitations that forbid the usage of that equation in this experiment. Having access to only a visible light spectrometer, collection of data on wavelengths outside the visible spectrum, most notably under $\lambda = 400 \text{ nm}$, are not available. From graph 1 it could be seen that the minimum point of the peak is in the 300-400 nm range, meaning that the specific absorbance at that point cannot be deduced, and hence the full width at half maxima cannot be recorded.

As a workaround, I compiled data published by Cytodiagnostics, a biotechnology company, which utilizes an extremely similar method to

⁸ ("Silver Nanoparticle Properties.")

⁹ (Desai, Rucha)

synthesize their own silver nanoparticle solutions. In particular, Cytodiagnostics published a data table indicating the relationship between average nanoparticle diameter and peak absorbance wavelength, seen in table 1:

Diameter (nm)	Peak SPR Wavelength (nm)
10	390-405
20	390-410
30	400-410
40	405-425
50	410-430
60	425-450
80	440-480
100	480-520



Table 1. Data table from Cytodiagnostics relating average nanoparticle diameter and peak absorbance wavelength¹⁰

This data was plotted against a scatter plot graph of average peak SPR wavelength to diameter of particle size. A trend-line was plotted against the graph and an equation was derived.

¹⁰ "Silver Nanoparticle Properties."

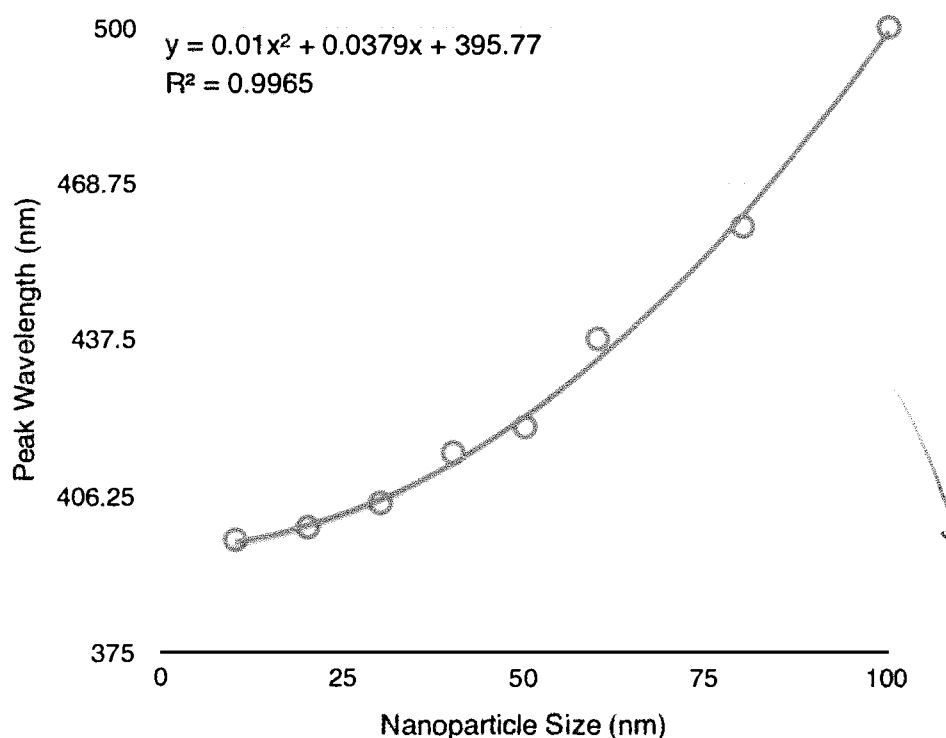


Figure 5. Trend-line on relationship between average nanoparticle diameter and average peak absorbance wavelength

A general equation for determining average nanoparticle diameter is thus deduced:

$$\lambda_{peak} = 0.01D^2 + 0.0379D + 395.77 \quad (1)$$

Where λ_{peak} is the peak absorbance wavelength and D is the diameter of the nanoparticles.

This equation seems to produce values be consistent with experimentations seen in literature.¹¹ The uncertainty is ± 10 nm; deduction of the uncertainty can be found in the appendix.

Selection and Controlling of Variables

Independent Variables

This experiment will consider two different independent variables.

The first independent variable is ionic strength. Ionic strength is defined to be $\frac{1}{2} \sum_{i=1}^n c_i z_i^2$, where c_i is the concentration of an ion and z_i is the ionic charge of the ion. In order to change the ionic strength of the added salt solution, the

¹¹ (Solomon, Sally D.)

concentration of the salt solution will be adjusted in increments of 0.2 M from 0.2 M solutions to 1.0 M solutions.


The second independent variable will be ionic radii. Ionic radii will be changed by using different salts from period 1: LiCl, NaCl, KCl and NH₄Cl. In this way, due to the salts having the same ionic charge, ionic strength would be the same between all the salt solutions.

Dependent Variables

This experiment will consider two different dependent variables.

The first dependent variable is the rate of aggregation of the silver nanoparticles after the addition of the salt solutions. To observe differences in rate, the relative absorbance at $\lambda = 407.0 \text{ nm}$ is taken once every 5 seconds for a period of one minute. As $\lambda = 407.0 \text{ nm}$ is close to the peak of the absorbance spectra and the peak flattens as the nanoparticle solution undertakes aggregation, determining the rate of falling relative absorbance serves as an analogous indication of rate of aggregation.

The second dependent variable is the overall degree of aggregation. Using a spectrometer, the absorption spectra of the nanoparticle solution is recorded at $t=60$ seconds. This final spectrum would then be used to determine average nanoparticle diameter using equation (1), allowing comparisons between different salt solutions and concentrations.



Controlled Variables

A selection of variables was controlled during this experiment in order to prevent aggregation:

The ratio of AgNO₃ and NaBH₄ must be kept at a 1:2 concentration ratio in order to maintain stability with the nanoparticles, otherwise aggregation could occur on its own. For this experiment, the concentrations of AgNO₃ and NaBH₄ solutions are 1 mM and 2 mM, respectively.¹²

Continuous stirring after adding the last drop of AgNO₃ into the NaBH₄ solution will also bring about aggregation. As such, stirring is stopped after addition of the last drop of AgNO₃ solution. In order to ensure that aggregation does not happen on its own after stirring, every freshly prepared Ag-NP solution batch is left untouched for one hour and monitored to ensure that aggregation does not occur. Batches in which aggregation is seen occurring are discarded.

¹² (Solomon, Sally D.)

The method used in this experiment allows for 40 mL batches of Ag-NP solutions to be made at a time. Due to the possible variability in dripping AgNO_3 time and random errors in measuring volume of reactants, nanoparticle diameters within different batches may be varied, potentially giving off slightly different absorbance spectra. To ensure consistent absorbance spectra across all trials, all successful batches are amalgamated into one large beaker, ensuring a consistent average nanoparticle diameter throughout all trials.

Procedure

Preparation of Ag Nanoparticle Solution

The preparation of silver nanoparticle solution is as follows. 0.019 ± 0.002 g of NaBH_4 was added to 250 ± 0.8 mL distilled water to make a 2 mM NaBH_4 solution, while 0.017 ± 0.002 g of AgNO_3 was added to 100 ± 0.3 mL to make a 1 mM AgNO_3 solution.

30 mL of NaBH_4 was transferred into a 125 mL Erlenmeyer flask with a magnetic stir bar and stirrer at the highest intensity with heat off. 10 mL of AgNO_3 was subsequently added drop-by-drop using a dropper at approximately a rate of one drop per second. The solution is noted to be in a golden-yellow colour after the AgNO_3 has been dripped and the magnetic stirrer is stopped.¹³

To ensure the silver nanoparticle solution does not further aggregate on its own, the now 40 mL batch is left sitting on the lab bench for one hour untouched. Batches in which aggregation still continues will turn visibly black, while batches in which aggregation does not occur will experience no visible colour change. Figure 6 shows the comparison between a failed batch and a successful batch.



¹³ (Solomon, Sally D.)

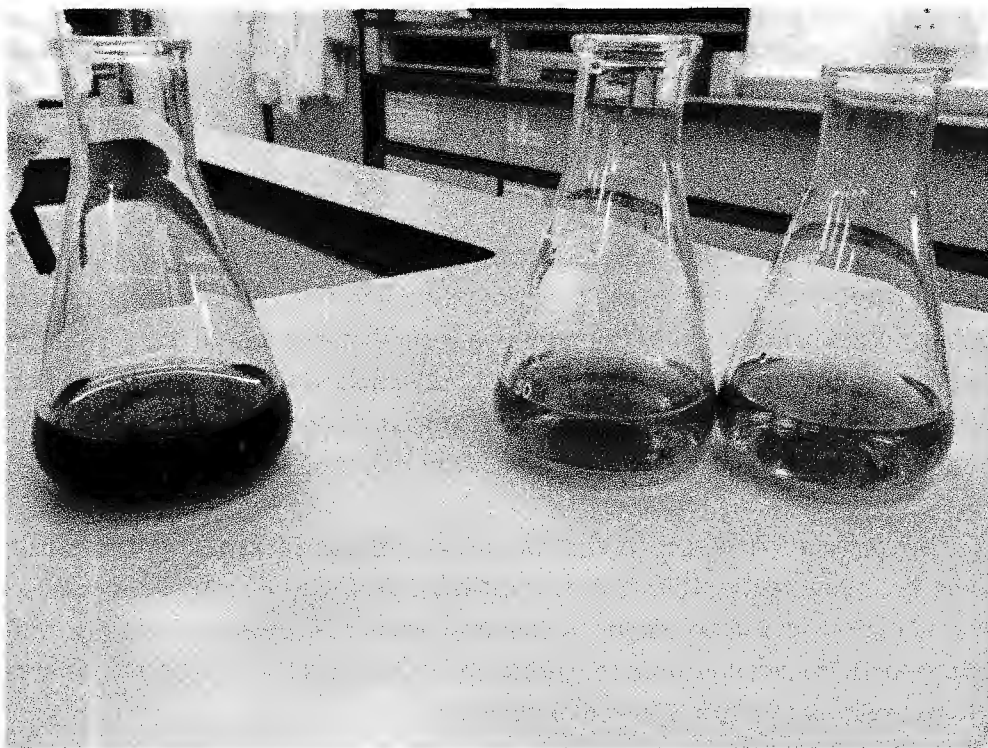


Figure 6. Comparison between failed silver nanoparticle batch (left) and successful silver nanoparticle batches (right)

In total, seven successful batches of silver nanoparticle solutions are made, a volume of 280 mL. The batches are then mixed into a 400mL beaker to ensure a consistent absorbance spectrum throughout all trials.

Main Experiment

Logger Pro 3.8.4 and Chinetek Vr Spectrovis Spectrometer-0910 was used in order to measure the absorbance spectrum from $\lambda = 403.4 \text{ nm}$ to 722.7 nm , the visible spectrum range. A cuvette with 3 mL of silver nanoparticle solution was placed into the spectrometer and its absorbance spectrum recorded as the base case. 0.2 mL of salt solution is then added to the cuvette and the absorbance spectrum of the new solution is taken one minute after the addition of salt solution.

Four different types of salts were used: LiCl, NaCl, KCl and NH_4Cl . For each salt, five different concentrations from 0.2 M to 1.0 M with increments of 0.2 M are used, each with an uncertainty of $\pm 0.05 \text{ M}$. Each salt and concentration combination undergoes four trials for a total of 80 absorbance spectra.

Chinetek Vr Spectrovis Spectrometer-0910 is unable to record data of full absorbance spectra over time, rendering it impossible to measure relative absorbance at $\lambda = 407.0 \text{ nm}$ every five seconds on its own. Logger Pro is capable, however, of *updating* the absorbance spectra at a rate of one per second, but not

recording the values of it. Screen-recording software Quicktime was thus used in order to record the changing values, overcoming Logger Pro's technical limitations and allowing data collection of relative absorbance over time.

Hypothesis

Literature suggests that an increase of concentration, and hence ionic strength, would increase the rate of aggregation and the degree of aggregation.¹⁴ A higher concentration would mean more ions that can shield the BH_4^- anions, allowing the nanoparticles to clump more. As such, my first hypothesis is that 1.0M would bring about a) the greatest amount and b) the quickest rate of aggregation, while 0.2M would bring about the least and slowest.

My second hypothesis is that the greater the ionic radius of the cation in the salt, the more aggregation that it will cause. As the ionic radius increases, the hydrated cation would be bigger in size and attract charges more easily, and so the nanoparticles can continue to clump. Table 2 shows the respective ionic radii length for each of the four different salts used:

Salt	Ionic Radius (pm)
LiCl	80
NaCl	100
NH_4Cl	175
KCl	160

Table 2. Ionic Radii of LiCl, NaCl, NH_4Cl and KCl¹⁵

From this, my hypothesis would then predict that both a) overall degree of aggregation and b) rate of aggregation would follow this decreasing trend: $\text{Rb} > \text{K} > \text{Na} > \text{Li}$.

Results and Discussion

Comparison between trials on Rate of Aggregation

Aggregation occurs nearly instantaneously after the addition of the salt solution. To compare the rate of this aggregation, the relative absorbance of 407.0 nm is taken per 5 seconds for one minute, as shown on Figures 7.1-7.4.

¹⁴ (Alzoubi, F. Y.)

¹⁵ (Kielland, Jacob)

Cations' Effect on Aggregation

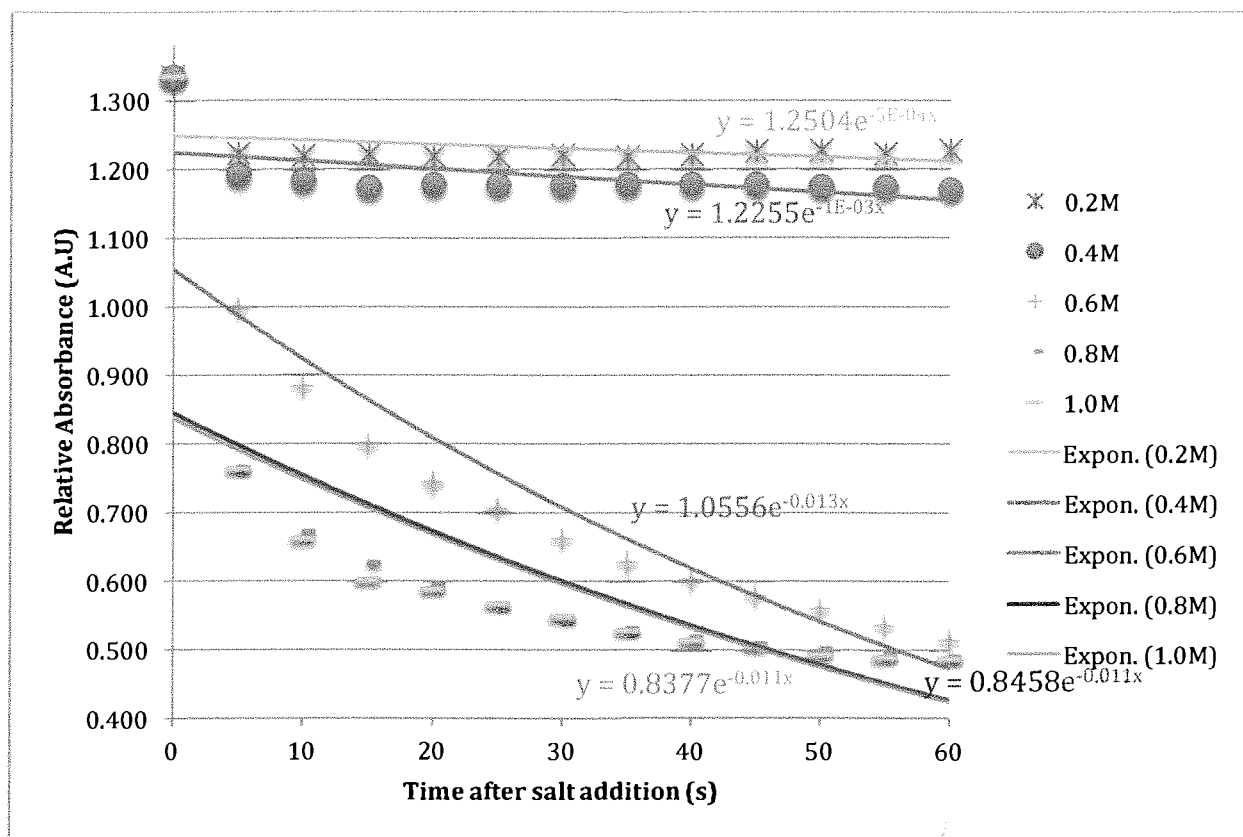


Figure 7.1 Rate of relative absorbance decrease at $\lambda_{nm} = 407.0$ nm for differing KCl concentrations

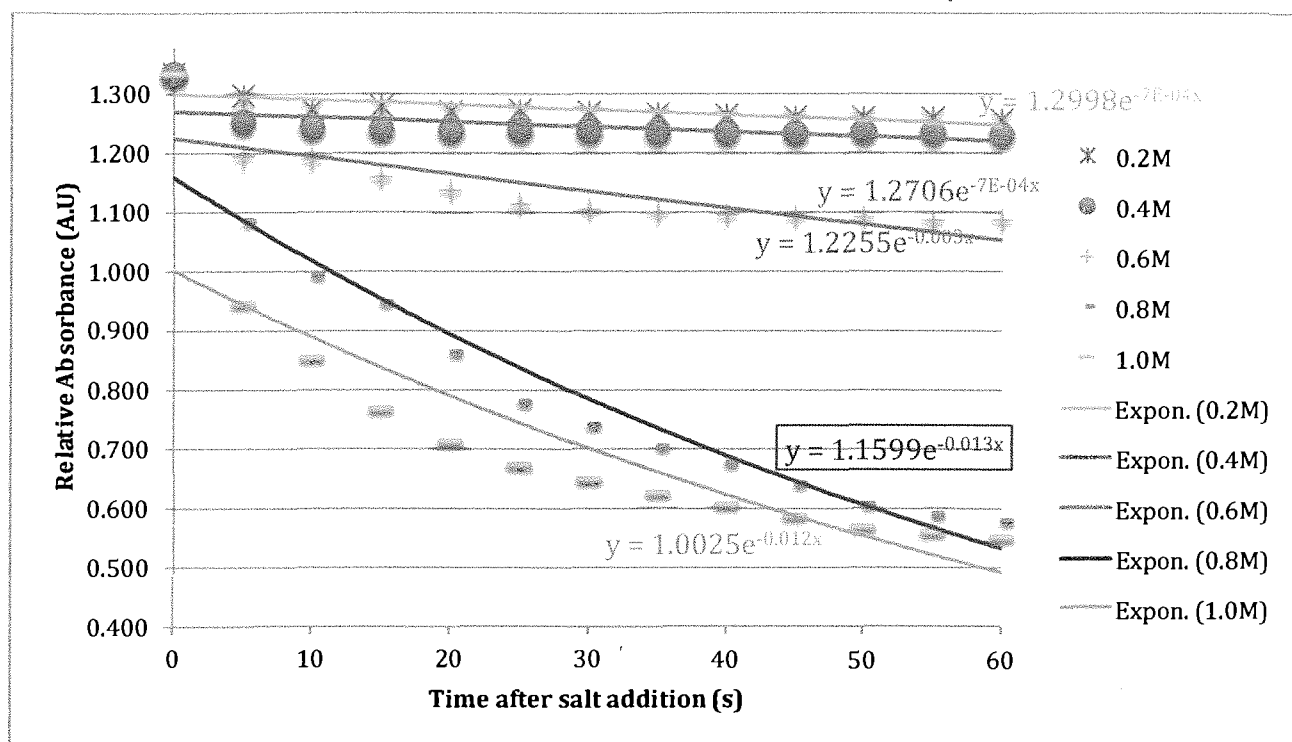


Figure 7.2 Rate of relative absorbance decrease at $\lambda_{nm} = 407.0$ nm for differing NaCl concentrations

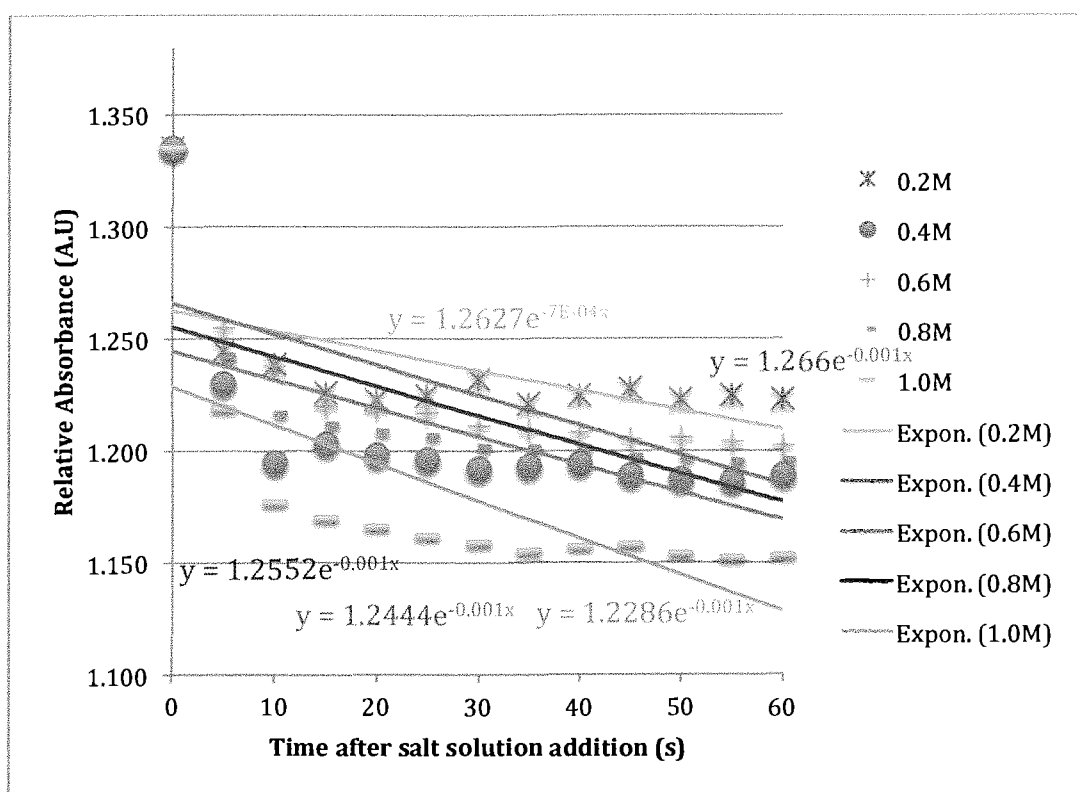


Figure 7.3 Rate of relative absorbance decrease at $\lambda_{nm} = 407.0$ nm for differing LiCl concentrations

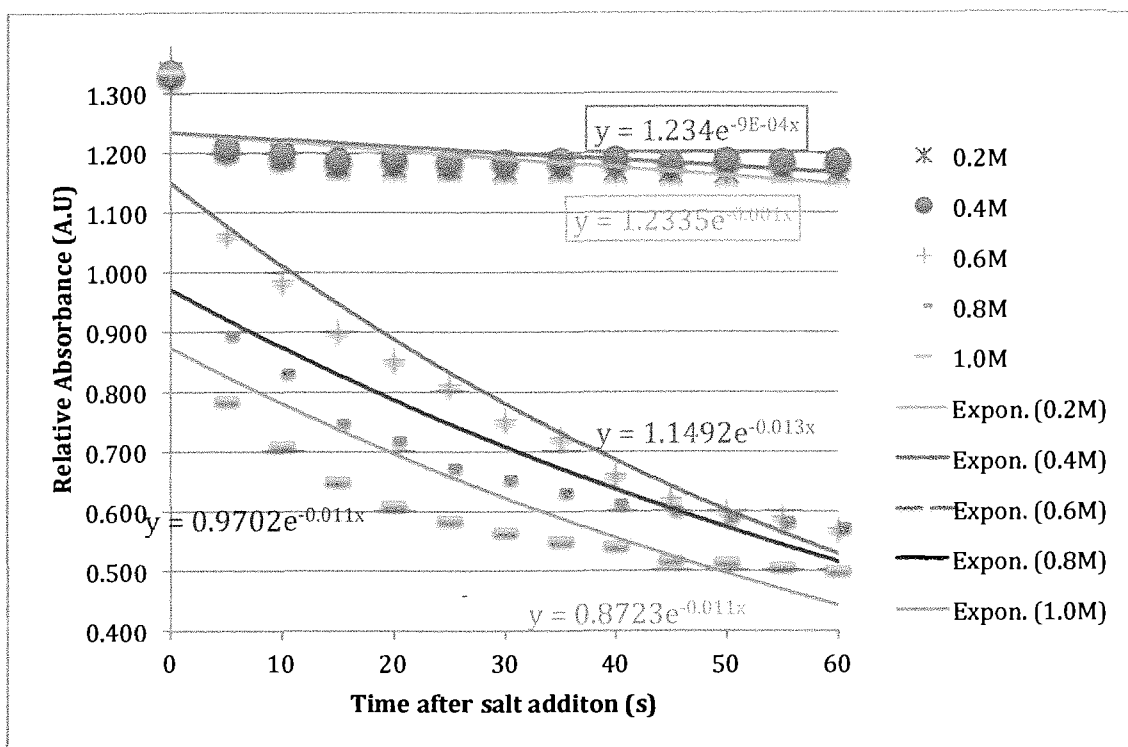


Figure 7.4 Rate of relative absorbance decrease at $\lambda_{nm} = 407.0$ nm for differing NH_4Cl concentrations

Figures 7.1-7.4 indicate that the rate of relative absorbance decreases exponentially as time increases for all trials. For example, in the first five seconds the relative absorbance for 1.0 M NH_4Cl at $\lambda_{nm} = 407.0 \text{ nm}$ decreases dramatically from 1.335 to 0.787, a drop of 0.548, but yet only decreases a further 0.284 to 0.503 for the remaining 55 seconds. An explanation for this exponential decrease may be due to the fact that as the nanoparticles aggregate, the increase in diameter would slow down due to the fact that more silver atoms are needed to increase the volume. Hence, it would make sense that the trend would decrease exponentially.

Figures 7.1-7.4 also indicate that an increase of ionic strength would also increase the rate of relative absorbance decrease. For all cases, 1.0 M have a relative absorbance drop to a greater extent in the same amount of time compared to their 0.2 M counterparts. For example, Figure 7.2 shows that 1.0 M NaCl has a drop of 0.388 in the first five seconds while 0.2 M only has a drop of 0.038. In addition, lower concentrations of salt solution added also seem stabilize more quickly than higher concentrations. For example, Figure 7.1 shows that relative absorbance in 0.2 M KCl solution added seems to plateau at around 1.225 after only 10 seconds, whereas the 1.0 M KCl solution added still seems to be decreasing after 60 seconds.

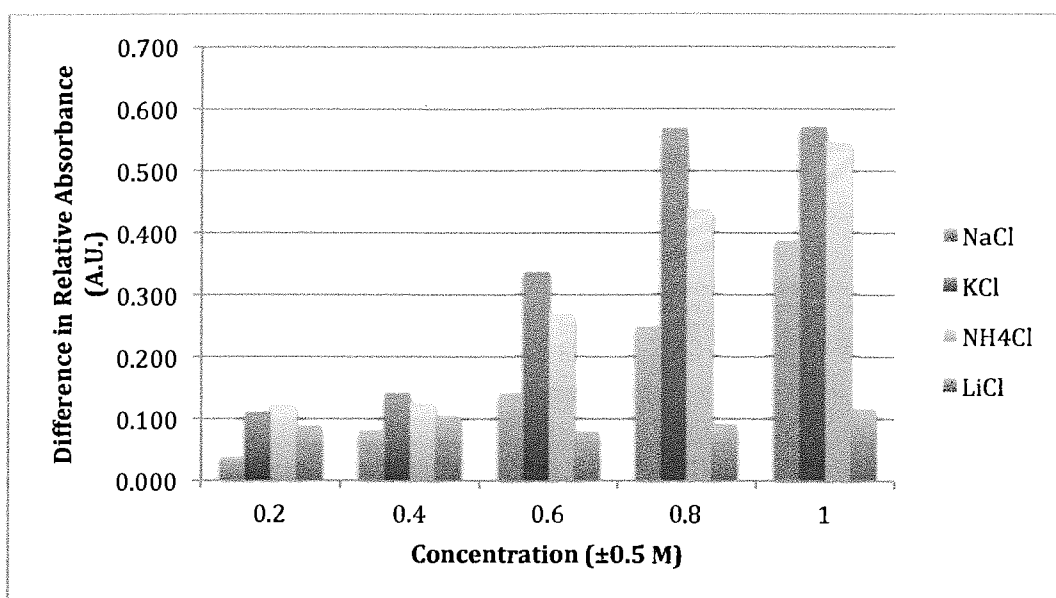


Figure 8. Difference in relative absorbance after first five seconds after addition of varying concentrations of salt solution

Figure 8 shows the difference in relative absorbance between readings after the first five seconds. A greater difference is indicative of a greater rate. This shows very clearly the increase in rate as the concentration increases,

overall supporting my hypothesis that an increase of ionic strength would result in a quicker rate of aggregation.

Figure 8 also allows the comparison between the different salt types in regard to their effect on rate of aggregation. It is clear that in general, addition of KCl causes the greatest difference in relative absorbance, followed by NH_4Cl , NaCl, and finally, LiCl. This seems to reject part b) of my second hypothesis, as I predicted that NH_4Cl would cause a greater rate of aggregation than KCl.

It is noted that for nearly all trials, the relative absorbance for $\lambda_{nm} = 407\text{nm}$ after 60 seconds has plateaued, an indication that aggregation has nearly or completely stopped altogether. This is used as a justification for using a time of 60 seconds to record the "final" absorbance spectra for the next section.

Comparison between trials after one minute of salt solution addition

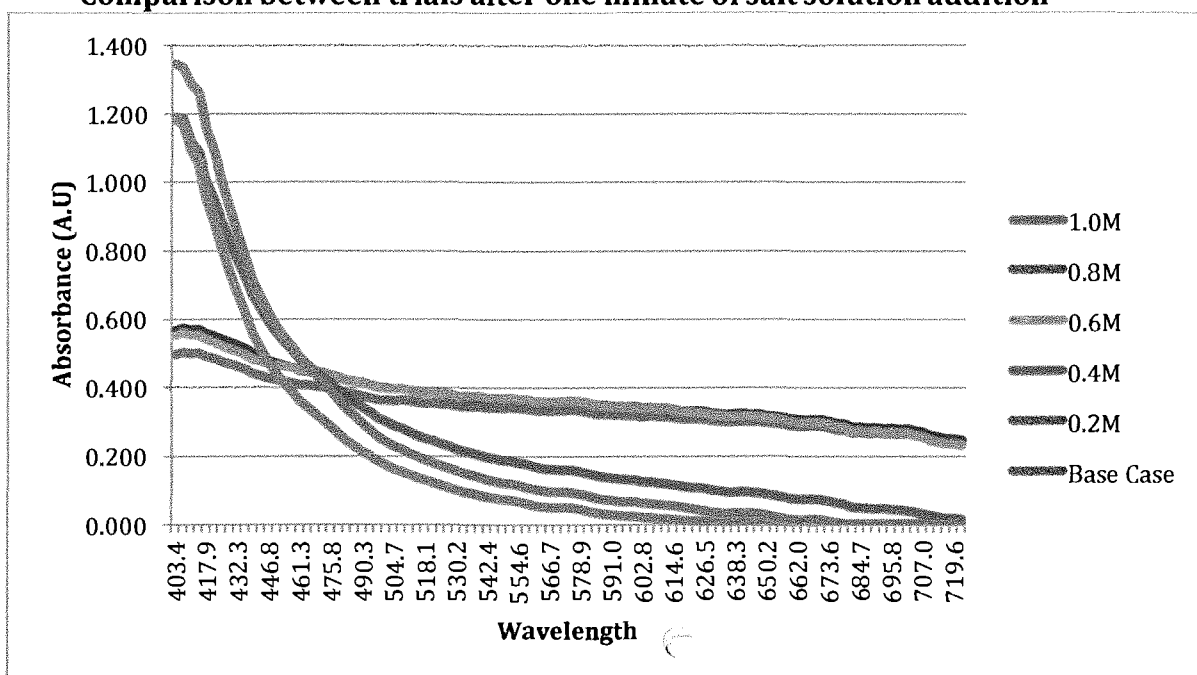


Figure 9.1: Absorbance spectra of silver nanoparticle solution after addition of various concentrations of NH_4Cl

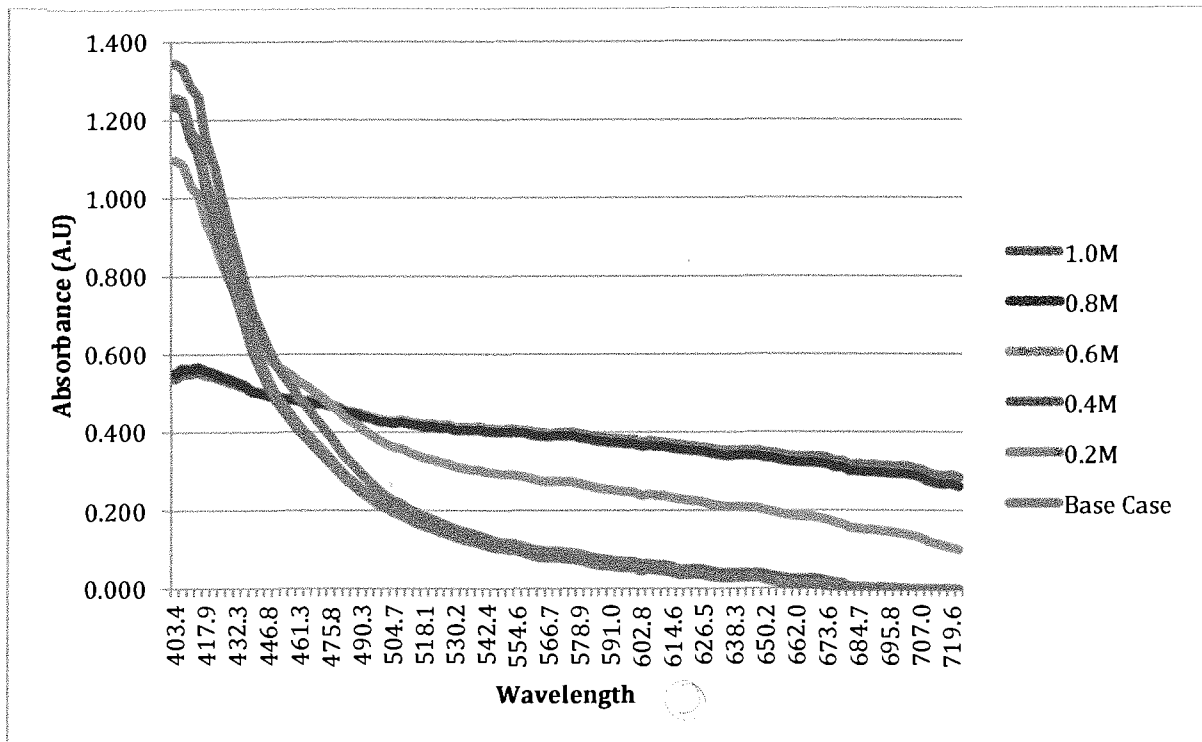


Figure 9.2 Absorbance spectra of silver nanoparticle solution after addition of various concentrations of NaCl

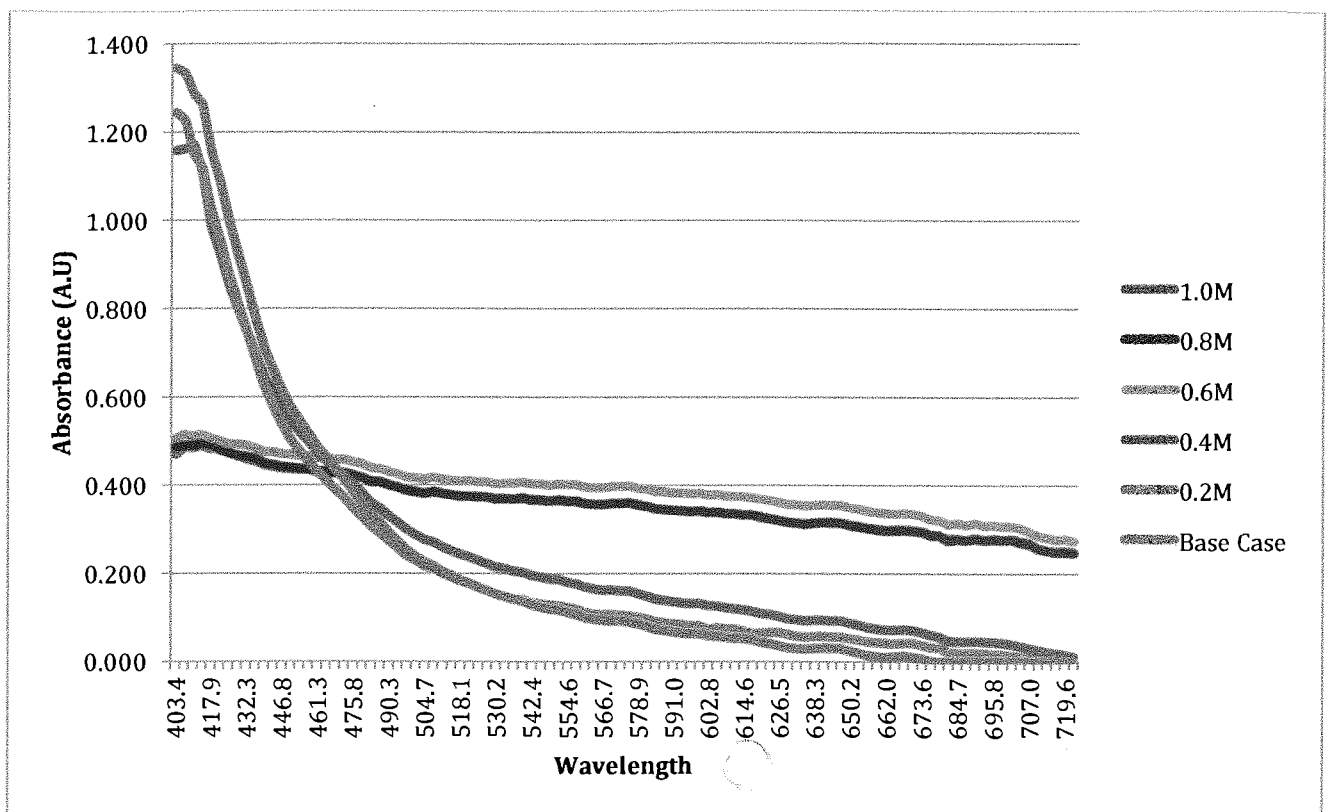


Figure 9.3 Absorbance spectra of silver nanoparticle solution after addition of various concentrations of KCl

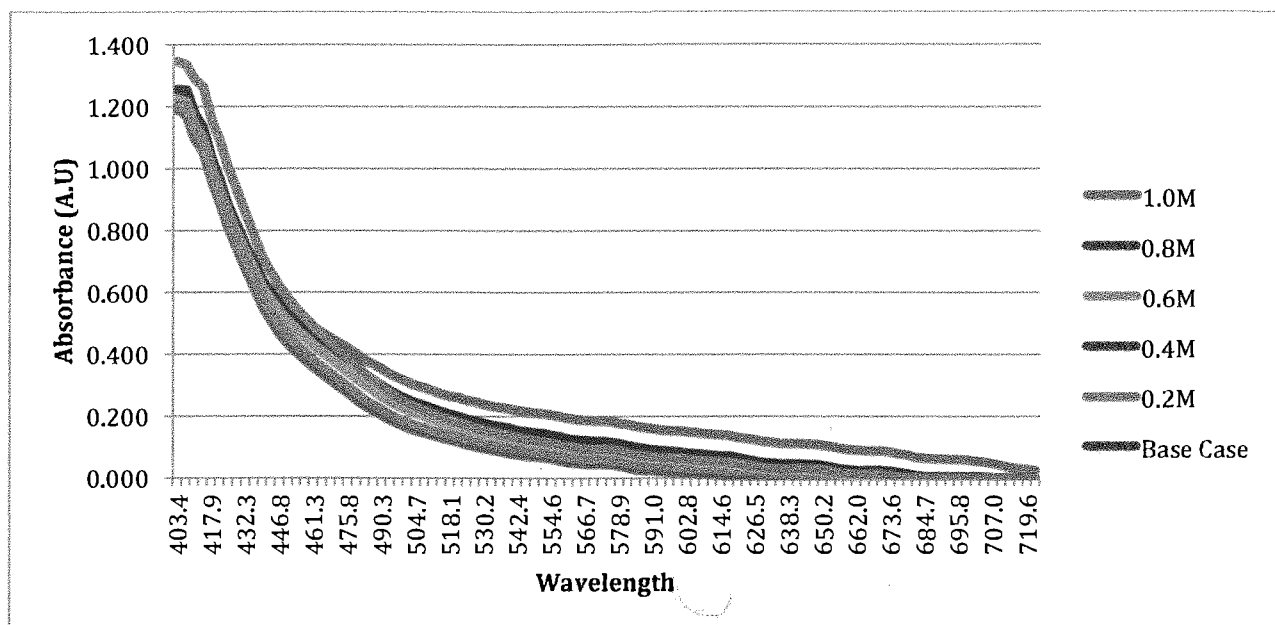


Figure 9.4 Absorbance spectra of silver nanoparticle solution after addition of various concentration of LiCl

Analyses of the absorbance spectra show a clear flattening of the peak as the concentration of the electrolyte solution increases. Figures 9.1 and 9.3 show that for NH_4Cl and KCl , there exists a large jump in peak flattening when concentration of salt solution is increased from 0.4 M to 0.6 M, while the same large jump exists from 0.6 M to 0.8 M for NaCl , shown in figure 9.2.

The extent of the peak flattening is considerably minimal for LiCl , indicated by absorption spectrum seen in figure 9.4, in which all absorbance spectra exhibit similar curves despite varying concentrations. However, there *does* exist a flattening of the peak, especially noticeable in the 1.0 M trials, in which the absorption spectrum flatten out more in comparison to other concentrations, especially in wavelengths above 500 nm. LiCl 's ability to shield charges seems to be far less adept, and hence aggregation is minimal.

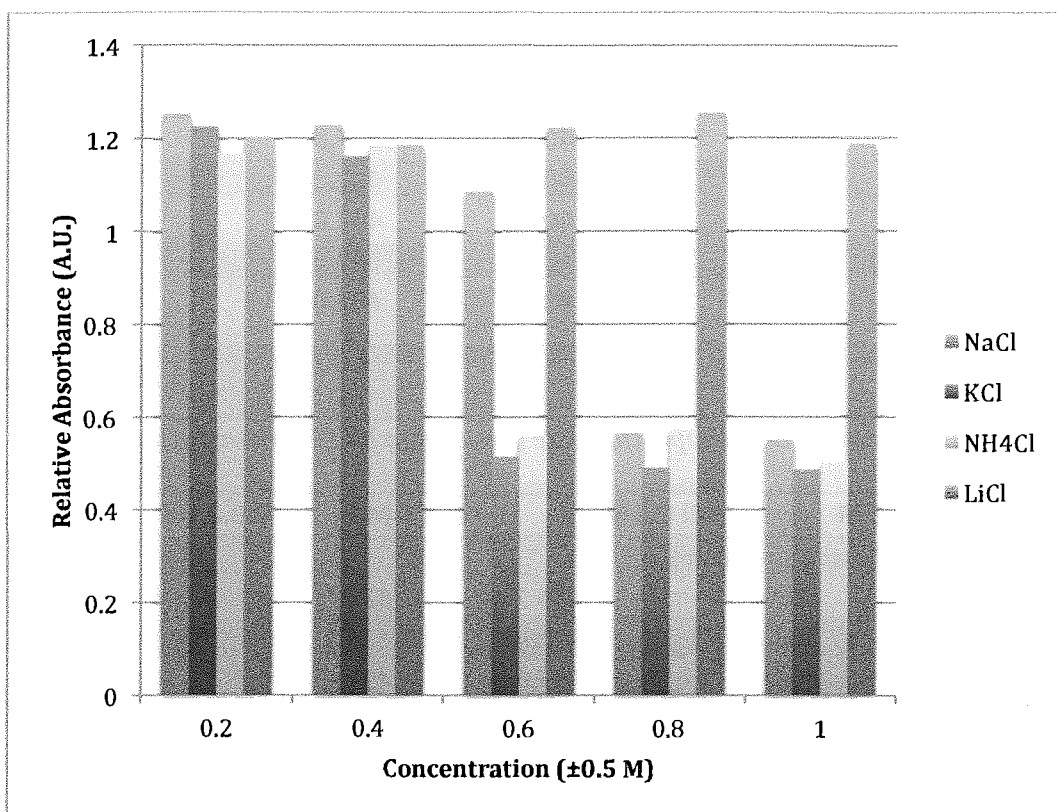


Figure 10. Average relative absorbance of silver nanoparticle solution at $\lambda = 407.0 \text{ nm}$ after addition of various concentrations of NaCl, KCl, NH₄Cl and LiCl

Figure 10 illustrates the extent of flattening between varying concentrations by comparing relative absorbance at wavelength $\lambda = 407.0 \text{ nm}$. As concentration increases from 0.4 M to 0.6 M for KCl solution, the relative absorbance drops dramatically from 1.163 to 0.515; similarly NH₄Cl decreases from 1.186 to 0.560. NaCl experiences a drop when increasing concentration from 0.6M to 0.8 M; its relative absorbance falls from 1.088 to 0.565. LiCl seems to be an anomaly, with the relative absorbance at $\lambda = 407.0 \text{ nm}$ staying somewhat constant. As noted before, however, there does seem to be a slight flattening of the peak as concentration increases, signifying the occurrence of aggregation. As such, this supports the hypothesis that an increase of ionic strength would lead to overall more aggregation.

Figure 10 also allows for a comparison between the three different salts. At 0.6 M, NaCl has a much higher relative absorbance with 1.088 compared to 0.515 and 0.560 for KCl and NH₄Cl, respectively, and hence it can be concluded that NaCl has a less overall aggregation effect than the other two salts. A comparison between KCl and NH₄Cl in relative absorbance shows that KCl has a lower relative absorbance in four out of the five concentrations (with exception of 0.2 M). It can be concluded from this that KCl has the greatest overall effect on overall degree of aggregation, followed by NH₄Cl, NaCl and finally LiCl.

Cations' Effect on Aggregation

	NaCl 0.2 M	NaCl 0.4 M	NaCl 0.6 M	NaCl 0.8 M	NaCl 1.0 M
Trial	Peak Absorbance (nm)				
1	403.4	403.4	407.0	407.0	414.2
2	403.4	403.4	407.0	407.0	407.0
3	403.4	407.0	407.0	407.0	407.0
4	403.4	403.4	407.0	414.2	414.2
Average	403.4	404.3	407.0	408.8	410.6
NP Size (nm) ±14	26	27	32	34	37

Table 3.1 Calculation on nanoparticle size for varying NaCl concentrations

	KCl 0.2 M	KCl 0.4 M	KCl 0.6 M	KCl 0.8 M	KCl 1.0 M
Trial	Peak Absorbance (nm)				
1	403.4	414.2	421.5	414.2	421.5
2	403.4	410.6	414.2	421.5	425.1
3	403.4	407.0	421.5	425.1	425.1
4	403.4	410.6	421.5	421.5	421.5
Average	403.4	411.5	419.7	420.6	423.3
NP Size (nm) ±10	26	37	47	48	51

Table 3.2 Calculation on nanoparticle size for varying KCl concentrations

	LiCl 0.2 M	LiCl 0.4 M	LiCl 0.6 M	LiCl 0.8 M	LiCl 1.0 M
Trial	Peak Absorbance (nm)				
1	403.4	403.4	403.4	403.4	403.4
2	403.4	403.4	403.4	403.4	403.4
3	403.4	403.4	403.4	403.4	403.4
4	403.4	403.4	403.4	403.4	403.4
Average	403.4	403.4	403.4	403.4	403.4
NP Size (nm) ±10	26	26	26	26	26

Table 3.3 Calculation on nanoparticle size for varying LiCl concentrations

	NH ₄ Cl 0.2 M	NH ₄ Cl 0.4 M	NH ₄ Cl 0.6 M	NH ₄ Cl 0.8 M	NH ₄ Cl 1.0 M
Trial	Peak Absorbance (nm)				
1	403.4	407.0	407.0	414.2	421.5
2	403.4	407.0	407.0	414.2	414.2
3	403.4	407.0	407.0	417.9	414.2
4	403.4	407.0	407.0	410.6	417.9
Average	403.4	407.0	407.0	414.2	417.0
NP Size (nm) ±14	26	32	32	41	44

Table 3.4 Calculation on nanoparticle size for varying NH₄Cl concentrations

As seen in tables 3.1, 3.2 and 3.4, NaCl, KCl and NH_4Cl is noted to also have a redshift as the concentration of salt solution increases. Silver nanoparticle solution had an average nanoparticle size increase from 26 nm to 37 nm after the addition of 0.2 mL 1.0 M NaCl. Solutions with 1.0M KCl added had an average nanoparticle size increase from 26 nm to 51 nm, while 1.0 M NH_4Cl had an average increase from 26 nm to 44 nm. This further supports the hypothesis that an increase of ionic strength would lead to overall more aggregation.

Qualitative observations indicate the process of aggregation. Addition of salt solution to silver nanoparticle solution causes the surface of the solution to quickly turn from light yellow to light grey, indicating the aggregation of nanoparticles. The colour then slowly trickles down through the cuvette, until all of the solution is of one uniform colour. Figure 11 shows the extent of colour change before and after the addition of salt solution.



Figure 11. Comparison of silver nanoparticle solution before addition of NaCl 1.0 M solution (right) and after addition (left)

Conclusion

Based on the data, an increase of ionic strength of salt solution added to silver nanoparticle solution would cause increase in both the overall degree of aggregation as well as the rate of aggregation. This is directly supportive of both parts a) and b) of my first hypothesis.

Salt	Ionic Radius (pm)	Hypothesized Rank	Overall Aggregation Rank	Rate of Aggregation Rank
LiCl	80	4	4	4
NaCl	100	3	3	3
NH ₄ Cl	175	1	2	2
KCl	160	2	1	1

Table 4. Ranking salts on their ability to bring about aggregation (1 is best, 4 is worst)

Both parts a) and b) of my second hypothesis, however, is rejected. Table 4 exemplifies my hypothesized ranking in aggregation potent compared to the actual observed results. The observation that KCl brings about the greatest overall aggregation, as well as a faster rate of aggregation, despite not having the greatest ionic radius is an indication that there is another, more prevalent, factor in bringing about aggregation.

Evaluation

Random Errors

Error for concentration in all salt solutions is ± 0.05 M. Measured relative absorbance when taken by the spectrometer seems to fluctuate even when measuring the same solution. The greatest source of random error is the nanoparticle size with an uncertainty of ± 10 nm, in some cases the relative uncertainty can reach over 50%, signifying large imprecision.

Systematic Errors

It is noticed that after the addition of the salt solution, many aggregated particles would become dense and sink, leaving a faint gradient from yellow to grey from the top to the bottom of the cuvette. As the spectrometer shines the light above the middle of the cuvette, more yellowish and smaller nanoparticles would have the absorbance spectra taken, and hence a systematic error occurs in which the peak wavelength of the solution measured is lower than reality. Despite this, the readings taken from the spectrometer is sufficient enough to deduce a noticeable trend.

The usage of micropipettes is also a source of systematic error. Due to limitations in supply, the tip of the micropipette is reused for all trials of the same salt and concentration. It is noted that occasionally a small bit of moisture is left inside the tip after ejection, meaning that the next injection of salt solution would have a small increase of salt solution added compared to previous trials, leading to extra aggregation. This is not a great source of error, as the small increase is extremely tiny and that all trials are similar to each other in their absorbance spectra.

Limitations

The Chinetek Vr Spectrovis Spectrometer-0910 was unable to measure wavelength below the values of $\lambda_{nm} = 400 \text{ nm}$, making it impossible to deduce the minima peak of the curve and hence making it unable to utilize Mie Scattering Theory in order to calculate the diameter of the nanoparticles, resulting in the deduction of a different, but less substantiated, formula in order to calculate the size with a relatively high uncertainty.

Second, the spectrometer measured wavelengths only in intervals of 4.6nm starting from $\lambda_{nm} = 403.4 \text{ nm}$, resulting in very imprecise estimations of nanoparticle size. The difference in average nanoparticle diameter between a peak of $\lambda_{nm} = 403.4 \text{ nm}$ and $\lambda_{nm} = 407.0 \text{ nm}$, for example, is 6 nm, which is a significant increase in size. Because of this imprecision, a more accurate comparison between different salts are impossible.

A solution for these limitations would be to use an UV-spectrometer instead of the basic spectrometer. The UV-spectrometer would be able to take readings below the $\lambda_{nm} = 400.0 \text{ nm}$ range, allowing for a fuller picture as to the absorbance spectra as the silver nanoparticle solution aggregates. In addition, UV-spectrometers are often more precise than normal spectrometers, allowing for better calculation and comparison of nanoparticle sizes. An UV-spectrometer would also allow for the full viewing of the peak, allowing one to utilize Mie Scattering Theory in order to much more accurately deduce the average size of the nanoparticles.

The scope of this experiment could also be expanded. A greater variety of concentrations should be used with smaller intervals between concentrations. For NH_4Cl and KCl , there seems to be a big difference in relative absorbance between 0.4 M and 0.6 M concentrations, while NaCl has a great difference in relative absorbance between 0.6 M and 0.8 M concentrations. In these instances the absorbance spectra both jump from a relatively defined curve into a flat plateau, easily seen in figures 3.1-3.3. A smaller interval between concentrations would provide a smoother transition.



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Appendix**Apparatus List**

- 125mL Erlenmeyer flask x7
- 250cm³ beaker x1
- 100cm³ beaker x1
- Magnetic stirrer x1
- Droppers x1
- Micropipette x1
- Logger Pro 3.8.4 x1
- Chinetek Vr Spectrovis Spectrometer-0910 x1
- Cuvette x1
- Screen-recording Software (Quicktime) x1

Deduction of nanoparticle diameter uncertainty

Uncertainty for the nanoparticle size is found by considering the maximum bound curve and the minimum bound curve from the values given in table 1.

Nanoparticle diameter (nm)	Highest Peak Wavelength (nm)	Lowest Peak wavelength (nm)	Average Peak wavelength (nm)
10	405	390	397.5
20	410	390	400
30	410	400	405
40	425	405	415
50	430	410	420
60	450	425	437.5
80	480	440	460
100	510	480	500

Table 5. Nanoparticle diameter and its highest, lowest, and average corresponding peak wavelength

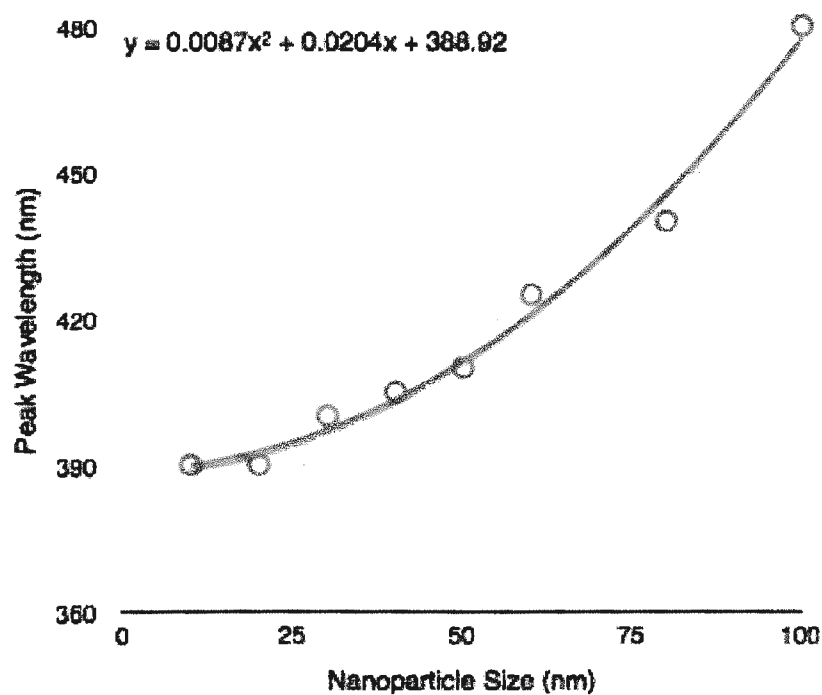


Figure 12.1 Trend-line on relationship between average nanoparticle diameter and highest peak absorbance wavelength

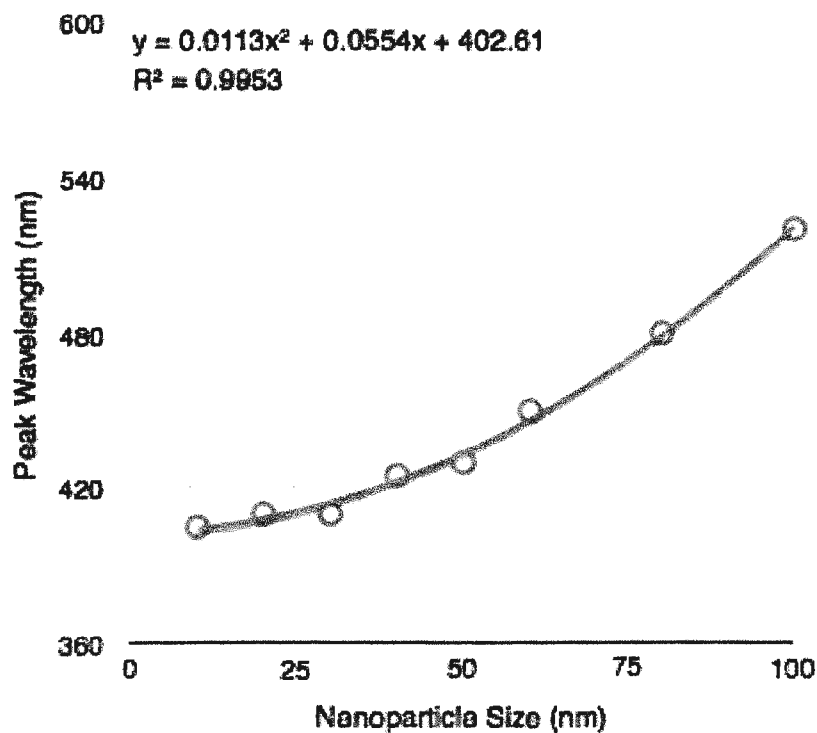


Figure 12.2 Trend-line on relationship between average nanoparticle diameter and lowest peak absorbance wavelength

Using the found trend-line equations and solving for $\lambda = 407.0 \text{ nm}$, the nanoparticle diameter is calculated to be between 18 nm and 44 nm from the minimum and maximum bound, respectively, with equation (1) giving a value of 32 nm. Therefore, the uncertainty is $\pm 10 \text{ nm}$, to one significant figure.

Related Data Tables

Seconds	0.2M AVG	0.4M AVG	0.6M AVG	0.8M AVG	1.0M AVG
0	1.335	1.335	1.335	1.335	1.335
5	1.224	1.193	0.998	0.765	0.763
10	1.221	1.185	0.884	0.672	0.662
15	1.223	1.175	0.799	0.627	0.602
20	1.220	1.179	0.744	0.595	0.589
25	1.220	1.178	0.705	0.567	0.567
30	1.221	1.178	0.662	0.547	0.549
35	1.219	1.179	0.628	0.531	0.529
40	1.222	1.179	0.603	0.519	0.514
45	1.227	1.179	0.580	0.509	0.505
50	1.228	1.175	0.561	0.502	0.494
55	1.223	1.175	0.536	0.494	0.489
60	1.228	1.170	0.515	0.490	0.487

Table 6.1 Relative absorbance at $\lambda_{nm} = 407.0 \text{ nm}$ after addition of differing KCl concentrations (Figure 7.1)

Seconds	0.2M AVG	0.4M AVG	0.6M AVG	0.8M AVG	1.0M AVG
0	1.335	1.335	1.335	1.335	1.335
5	1.297	1.254	1.194	1.087	0.947
10	1.273	1.243	1.189	0.995	0.855
15	1.279	1.240	1.160	0.949	0.769
20	1.269	1.238	1.137	0.864	0.713
25	1.272	1.239	1.115	0.780	0.674
30	1.268	1.237	1.105	0.741	0.649
35	1.265	1.235	1.100	0.705	0.626
40	1.263	1.235	1.096	0.677	0.606
45	1.260	1.234	1.094	0.641	0.587
50	1.259	1.236	1.092	0.606	0.568
55	1.258	1.234	1.087	0.590	0.559
60	1.255	1.231	1.088	0.578	0.550

Table 6.2 Relative absorbance at $\lambda_{nm} = 407.0 \text{ nm}$ after addition of differing NaCl concentrations (Figure 7.2)

Seconds	0.2M AVG	0.4M AVG	0.6M AVG	0.8M AVG	1.0M AVG
0	1.335	1.335	1.335	1.335	1.335
5	1.210	1.209	1.064	0.896	0.787
10	1.196	1.198	0.985	0.833	0.712
15	1.180	1.187	0.901	0.748	0.652
20	1.179	1.189	0.852	0.719	0.612
25	1.178	1.184	0.81	0.674	0.587
30	1.173	1.185	0.751	0.654	0.568
35	1.175	1.187	0.721	0.632	0.552
40	1.172	1.189	0.66	0.614	0.544
45	1.169	1.182	0.62	0.602	0.52
50	1.167	1.187	0.599	0.59	0.517
55	1.172	1.185	0.589	0.582	0.509
60	1.169	1.186	0.57	0.574	0.503

Table 6.3 Relative absorbance at $\lambda_{nm} = 407.0 \text{ nm}$ after addition of differing NH_4Cl concentrations (Figure 7.3)

Seconds	0.2M AVG	0.4M AVG	0.6M AVG	0.8M AVG	1.0M AVG
0	1.335	1.335	1.335	1.335	1.335
5	1.245	1.230	1.255	1.243	1.219
10	1.239	1.195	1.238	1.217	1.177
15	1.226	1.203	1.220	1.212	1.170
20	1.223	1.198	1.219	1.209	1.166
25	1.225	1.196	1.217	1.207	1.162
30	1.232	1.192	1.211	1.202	1.159
35	1.221	1.193	1.209	1.201	1.155
40	1.225	1.194	1.208	1.201	1.157
45	1.228	1.189	1.205	1.197	1.158
50	1.223	1.187	1.206	1.197	1.154
55	1.225	1.186	1.204	1.195	1.152
60	1.223	1.189	1.202	1.196	1.153

Table 6.4 Relative absorbance at $\lambda_{nm} = 407.0 \text{ nm}$ after addition of differing LiCl concentrations (Figure 7.4)

	NaCl	KCl	NH ₄ Cl	LiCl	
Concentration (M)	Difference in Relative Absorbance (A.U)				
0.2 ±0.05		0.038	0.111	0.125	0.090
0.4 ±0.05		0.081	0.142	0.126	0.105
0.6 ±0.05		0.141	0.337	0.271	0.080
0.8 ±0.05		0.248	0.570	0.439	0.093
1.0 ±0.05		0.388	0.572	0.548	0.116

Table 7. Difference in relative absorbance after first five seconds after addition of varying concentrations of salt solution (Figure 8)

	NaCl	KCl	NH ₄ Cl	LiCl
Concentration (M)	Relative Absorbance (A.U)			
0.2 ±0.05	1.255	1.228	1.169	1.206
0.4 ±0.05	1.231	1.163	1.186	1.188
0.6 ±0.05	1.088	0.515	0.560	1.225
0.8 ±0.05	0.565	0.490	0.574	1.256
1.0 ±0.05	0.550	0.487	0.503	1.19

Table 8. Average relative absorbance of silver nanoparticle solution after addition of various concentrations of NaCl, KCl, NH₄Cl or LiCl (Figure 10)